Indian J. Phys. **65B** (5), 459-465 (1991)

Carotenoids : Novel biomolecules of potential device applications

Prabir Pal and T N Misra
Department of Spectroscopy, Indian Association for the Cultivation of Science, Jadavpur, Calcutta-700 032, India

Abstract : The presence of various adsorbed gases increases the semiconduction current of carotenoids. Among different carotenoids crocetin is the most sensitive sensor for ethanol vapour. Thin film surface cell shows faster response and recovery. Very high photoconductive response is obtained for crocetinaldehyde and can be used for optical switching devices. Carotenoids are capable of forming charge-transfer complex with iodine. About seven order of current enhancement is observed for lycopene-iodine CT complex. A Mg/lycopene-iodine CT complex/C solid state battery is developed. Battery parameters indicate its applicability for microgadget energizer.

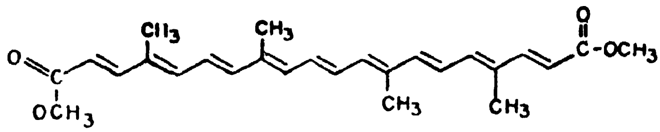
Keywords : Organic semiconductors, vapour adsorption, charge-transfer complexes, current-voltage characteristics, open circuit voltage.

PACS Nos : 87.10. +e, 87 15. Mi, 72.80. Le

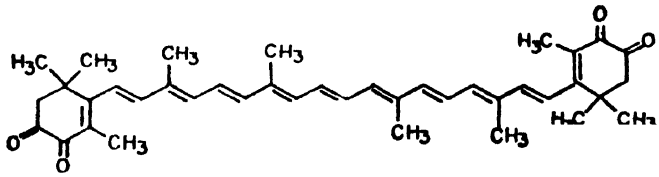
1. Introduction

Carotenoids constitute the second major pigment found in all autotropic plants. Their presence in plant leaves along with chlorophylls and also in green and purple photosynthetic bacteria indicate their involvement in photosynthesis (Rosenberg 1961, 1966a, Goodwin 1980). Free and protein bound carotenoids are found in certain loci of undisputed importance such as in the rod and cone layers of eye and in the olfactory epithelium of animals and of human beings. Visual pigment rhodopsin is a carotenoid 11-cis retinal bound to an apoprotein opsin by a protonated Schiff-base to the terminal amino group of lysine residue. Photoisomerisation of retinal is the basic process of our visual sensory perception. Another sensory perception in which carotenoids are involved is olfaction (Rosenberg *et al* 1968).

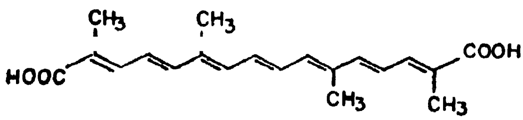
In Figure 1 some common carotenoids are shown. These are conjugated π-electronic chain molecules with alternate single and double bonds. The conjugated π-electronic structure gives these compounds the properties of semi- and photoconductors in the crystalline state. Their unique semi- and photoconductive properties lead to the possibility that these materials can be used in the development of some useful devices such as gas sensors, optical switching devices, organic metals and solid state battery. In this paper we report the experimental results of our studies in the context of device development.



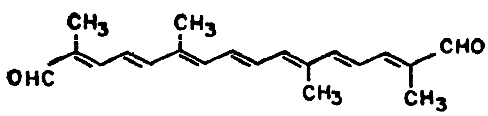
1. Methylbixin



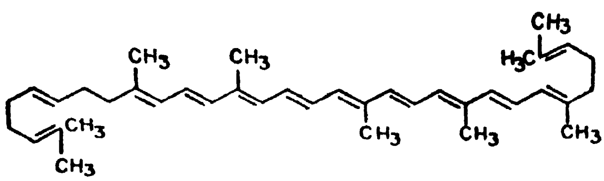
2. Astacin



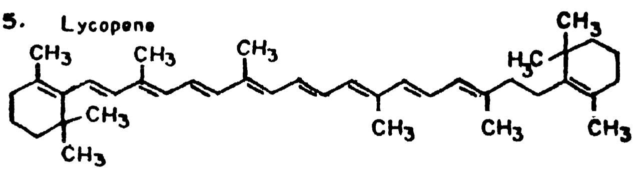
3. Crocetin



4. Crocetinaldehyde



5. Lycopene



6. β-carotene

Figure 1. Chemical structure of some linear conjugated polyenes.

2. Experimental

Highly pure carotenoids used in this investigation were obtained as a gift from the Hoffman-La-Roche Co., Switzerland and were used without further purification after checking the purity of the sample by absorption spectroscopy. The sample was taken in a sandwich cell with stainless steel and SnO_2 coated glass electrodes for conductivity measurement. The cell was placed in a suitably designed conductivity chamber (Mallik *et al* 1979) with a quartz window for photoconductivity studies. For current measurement, Keithley 617 programmable electrometer was used. This electrometer was also used as a voltage source to apply d.c. voltage. Temperature measurement was made using a copper-constantan thermocouple. A 100 watt xenon lamp was used for steady state photoconductivity work. A Shimadzu spectrophotometer (model No. 210A) was used to run the absorption spectrum. The sandwich cell thickness and area were maintained at 0.005 cm and 0.25 cm^2 respectively. Several measurements were made in order to ensure reproducibility of results both in vacuum and also in an atmosphere of dry nitrogen.

3. Results and discussion

3.1. Gas sensors :

Carotenoids are semiconductors in the solid state. The interesting aspect about the semiconducting properties of the carotenoids is that it is very sensitive to the ambiant atmosphere. As the ambiant gas molecules get adsorbed on the carotenoid crystals, its conductive properties change significantly. It has been reported (Rosenberg *et al* 1968) that presence of nitrogen dioxide, hydrogen sulphide, ammonia, methanol, nitric oxide, acetone etc. enhances the conductivity of β-carotene by 10^4-10^6 times but only moderate increase is observed with methyl acetate, nitrous oxide etc. With nitrogen, hydrogen and helium gas there is no significant change. On methyl acetate vapour adsorption vitamin A alcohol cell senses methyl acetate vapour very efficiently but only low response is obtained in β-carotene cell.

Table 1 shows our results on ethanol gas sensors with carotenoids. After trying a number of carotenoids, crocetin is found to be most sensitive biomaterial for alcohol sensing.

Both thin film sandwich cell and surface cell have been studied. Vacuum deposited thin film surface cell sensor shows very fast response and recovery. The active layers used in our sensors have not yet been optimised. Future work to optimise sensor characteristics is needed and low noise, IC-compatible FET device structures is to be designed and fabricated. The deposition conditions for our thin films are completely compatible with such structures. The unique electrical properties of the films are a result of the film morphology associated with our specific deposition approach.

12

Thus different polyenes respond differently to different gases as regards their electrical conductivity. By using different polyenes, it is thus possible to develop a sensor specific to a particular gas.

Table I. Ethanol sensors with carotenoids. Sensor at 25°C. Partial vapour pressure of alcohol is 80 mm.

Sl. No.	Carotenoid	σ_A/σ_V Sensitivity
1	Vitamin A alcohol	3×10^{3}
2	Vitamin A acetate	$2\times10^{[illegible]}$
3	β-Apo-8′ carotenal	5×10^{3}
4	Astacin	4×10^{5}
5	Methylbixin	1×10^{3}
6	Crocetin	8×10^{5}

σ_A = conductivity after adsorption of alcohol.
σ_V = conductivity in dry nitrogen atmosphere.

3.2. *Optical switching devices* :

The basic properties required for an optical switching device is that a high resistance material becomes conducting due to the action of light. Some of the polyenes possess this properties to a good extent. The current-voltage characteristics of dark and photocurrent of crocetinaldehyde crystals in a sandwich cell are shown in Figure 2. If one chooses a working voltage of 40 V, it is seen that the current increases 10^4 times due to the action of light. It is possible to design the cell with larger surface area and smaller thickness to enhance the photoconductivity of the sandwich cell by a few order of magnitude more. These materials can, therefore, be used to develop an optical switching device.

3.3. *Organic conductors* :

The fundamental requirement of high conductivity is partially filled conduction band i.e., mixed valence state. This situation is not met in carotenoid crystals. These are semiconductors with a energy band gap, an empty conduction band and a partially filled valence band. However, this situation can be changed by forming charge-transfer complexes. Some organic charge-transfer salts, where the donor and the acceptor molecules form segregated stackings in the lattice and the charge transfer between them is partial, are highly conducting (Torrance 1985). The other mechanism of high conductivity in organic solid in intersoliton hopping which makes doped polyacetylenes and related conjugated polymers highly conducting (Kivelson 1981). Like polyacetylenes, polyenes are also conjugated π-electronic system with alternate single and double bonds in the main chain. One can find a carotenoid with favourable end groups or tailor a caro-

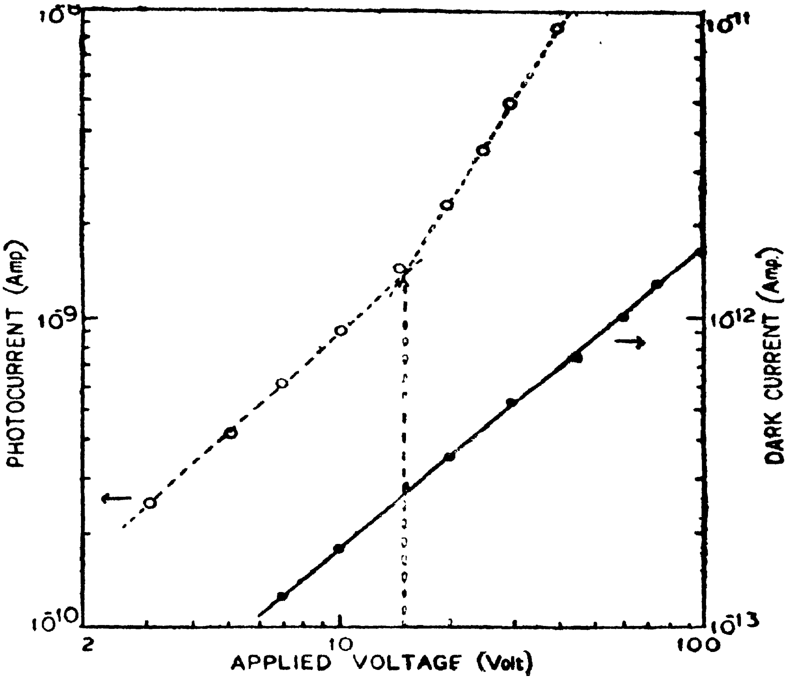


Figure 2. I-V characteristics of crocetinaldehyde in dark and on illumination. (——) represents dark and (- - -) represents for photoconductivity.

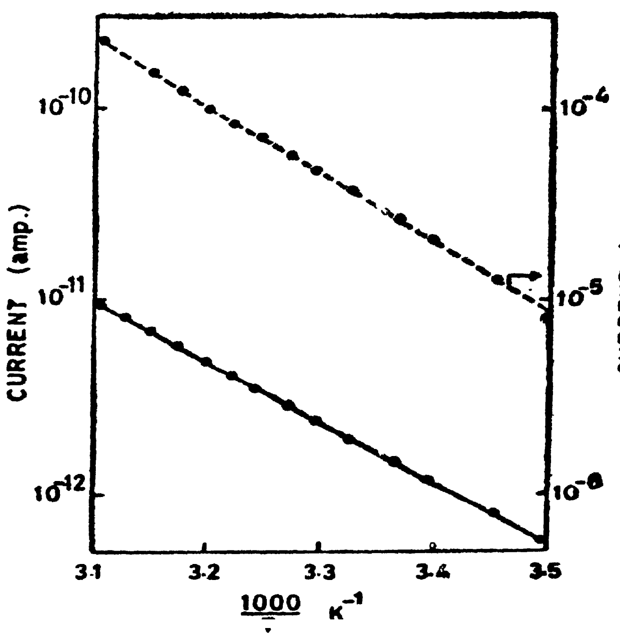


Figure 3. Arrhenius plots for pure lycopene and lycopene-iodine complexes. Solid lines represent pure lycopene and dashed lines represent lycopene-iodine complexes.